

SCIENCE FOR GLASS PRODUCTION

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EFFECT OF WATER ON THE STRUCTURE AND PROPERTIES OF GLASS (REVIEW)

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It is shown that OH groups affect the technological and physical-chemical properties of glass. The importance of and need for research in this direction are substantiated by the facts that new artificial and natural raw materials are now being used and that adding oxygen to burn fuel changes the composition of the atmosphere in the glassmaking furnace.

In glass technology, water has never been regarded as a component of the batch even if it is present in quantities above 1 – 2%. It has never been viewed as an oxide constituent of oxide glasses. Descriptions of glass production mention water in passing without giving any special attention to it, and its value for the synthesis process where it plays an important role in the formation of glass is underestimated. Nevertheless, water deserves to be called a “raw material” for glass production.

Many salient features of the synthesis and structure of glass can be misunderstood if the role of water is neglected. Present in the batch as a component moisture participates strongly in the reactions occurring at the silicate formation stage. It is well known that the best conditions for the mixing, melting, clarification, and production processes in glass making obtain with moisture content 4.0 – 4.5% [1].

The following could be sources of OH groups in glass:

- structure-free, adsorption, and hygroscopic water [2], present in moist raw materials and moistened batch;

- chemically bound water present in the raw materials (natural soda, crystal hydrates, hydroxides: NaOH, Al(OH)₃, and others) and in amorphous forms of silica (perlite, diatomite, tripoli, and others);

- water formed when fuel is burned and entering together with air into the gas atmosphere above the glass melt.

The amount of H₂O present in the atmosphere inside the furnace depends strongly on the hydrogen content in the fuel. Switching to blowing oxygen also increases the concentra-

tion of water vapor in the atmosphere inside the furnace; this increases the content of OH groups in the glass. Comparing the equilibrium solubility of various gases in silicate melts has established that alkali-containing aluminum-magnesium-silicate compositions are supersaturated with CO₂ by more than a factor of 1000, while SO₂ forms with the glass mass a supersaturated solution with concentration 1 – 2 orders of magnitude higher than the equilibrium value, but only at temperatures above 1300°C. The concentration of water vapor in the glass mass is close to the equilibrium concentration [3, 4]. At temperatures which are low enough so that an OH group can combine with a hydrogen atom to form H₂O, OH groups can participate in water formation in the melt [1].

IR spectroscopic studies of glasses suggest that water is present in glass in the form of OH groups and in an adsorbed form [5 – 7].

Commercial glasses ordinarily contain from 0.02 to 0.06%² OH groups, and natural glasses such as mica contain up to 1% [8]. New data obtained from x-ray fluorescence analysis and IR spectroscopy show that commercial sheet glass contains from 0.013 to 0.016% H₂O [9], and container glasses of different colors contain from 0.030 to 0.042% [10]. Quartz glass obtained by the vapor-phase method from silicon tetrachloride or tetrahydroxysilane contains 0.1 – 0.3% OH groups [11, 12].

Some glasses exhibit a different temperature dependence of water absorption. For example, the amount of absorbed water in SiO₂ – R₂O₃ – B₂O₃ – Na₂O and SiO₂ – R₂O₃ – CaO – MgO – Na₂O glasses decreases as temperature in-

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² Hear and below, unless otherwise state, the mass content.

creases but it increases in $\text{SiO}_2 - \text{PbO} - \text{K}_2\text{O} - \text{Na}_2\text{O}$ glasses [13].

Besides the glass composition and temperature, the conditions under which glass is made also affect the water content of glass. It has been determined that the content of OH groups is as follows (%): 0.030–0.040 in container glass and 0.025–0.040 in sheet glass for ordinary gaseous glassmaking; 0.015–0.020 for electric glassmaking; and, up to 0.050–0.060% for oxygen glassmaking [14].

M. J. Burger clearly illustrated the mineralizing effect of OH groups by ruptures of Si–O–Si bridges, which give rise to the high viscosity of “dry” silicate melts and glasses. An OH group replaces an oxygen atom occupying a vertex of the silicon–oxygen tetrahedron and, similarly to Na^+ , decreases the degree of connectivity of the silicon–oxygen framework. Each bridge oxygen atom must be replaced by two OH groups in order to compensate the free valences of the two silicon atoms on the opposite ends of the previously existing bridge. The “fluxing” nature of the OH groups is manifested in the fact that the continuous silicate network breaks up into separate, small, islands [1].

The fact that the O^{2-} ions in silicate structures can be replaced with $(\text{OH})^-$ ions can be proved from the crystal-chemistry standpoint. Crystal chemistry explains this substitution by assigning to both $(\text{OH})^-$ anions bound with a silicon ion the same spherical shape and the same radius, equal to 0.133 nm, very close to the radius of bivalent O^{2-} — 0.146 nm [15].

The OH groups in multicomponent glasses can be in direct proximity to a nonbridge oxygen atom $\equiv\text{Si}-\text{O}^-$, bound with a modifier ion. In this case a hydrogen bond can arise between the proton in the OH group and the nonbridge oxygen atom $\equiv\text{Si}-\text{O}-\text{H} \cdots \text{O}^--\text{Si}\equiv$, and this hydrogen bond weakens the O–H bond. Hydrogen bonds break when glass is heated. Stronger hydrogen bonds start to undergo thermal dissociation at higher temperatures. The hydrogen-bond strength in glass decreases in the following order: potassium-, sodium-, and calcium-silicate glasses.

Studies of how the introduction of various oxides into glass affects the strength of hydrogen bonds have shown that it remains unchanged when Al_2O_3 is added to alkali-silicate glass, though the number of hydrogen bonds decreases because the concentration of nonbridge oxygen atoms decreases. The hydrogen bonds in sodium-aluminosilicate glass are weaker than those in potassium-aluminosilicate glass. When a divalent-metal oxide is introduced into potassium-silicate glass the strength of hydrogen bonds changes depending on the strength of the field of the divalent cation.³ For example, the bond strength decreases as this field becomes weaker [5].

For binary alkali-borate glasses containing lithium, sodium, and potassium oxides, the water content in the glass

decreases as the glassmaking time increases [16]. The conditions of synthesis influence the ratio of the free and bound hydroxyl groups [17].

Water plays an important role in the structure of glasses. Even when present in only trace amounts (approximately $10^{-2}\%$) water has a strong effect on the technological and physical-chemical properties of glass. The few data that are available show that water accelerates the physical-chemical reactions forming silicates and decreases the temperatures at which these reactions start and proceed. The appearance of the first sections of a liquid phase in the mixture decreases the viscosity and the surface tension of the glassy part of the batch, facilitating the wetting of the solid particles by the melt and thereby increasing the rate of their dissolution, increases the surface of the reacting substances many-fold, decreases the glass-formation temperature, and decreases the mechanical strength.

In spite of all the publications on the role of water in glass-formation processes, the nature of the effect of water on many properties of glass is still not fully understood. The first works in this field focused on decreasing as much as possible the amount of water present as an impurity [18, 19], for example, to improve the optical characteristics of glasses, especially in the IR range. In recent works, water has been intentionally introduced in large amounts into the glass mass to obtain materials with unusual characteristics and to study how the water affects their structure and properties [20–23].

The viscosity varies directly as the number of oxygen bridges and inversely as the number of OH groups in the melt [1, 24]. For all characteristic viscosity points of a glass from $10^{7.6}$ to 10^{13} Pa·sec, an increase of the content of hydroxyl groups gives rise to a corresponding temperature decrease ranging from 2 to 4°C, though no obvious differences in the formation process for glasses with different OH-group content was observed [14].

The change of the vitrification temperature of glass per unit change of the molar content of H_2O increases for different glasses in the following order: lithium → sodium → potassium. Differential thermal analysis has established that as the content of residual water increases, the glass-formation and crystallization temperatures of potassium metaphosphate decrease by $\Delta t_g = 40^\circ\text{C}$ and $\Delta t_{cr} = 80^\circ\text{C}$, respectively.

Water determines the high absorption in the near-IR range of the spectrum. The stretching vibrations of the OH groups give rise to an absorption band that peaks in the range 2700–2900 nm. For example, the OH groups in quartz glass correspond to absorption bands with a maximum at 2730 nm and weaker bands with maxima at 1400 and 2400 nm [25]. In multicomponent systems with hydrogen bonds arising as a result of the interaction of the hydrogen in OH groups with nonbridge oxygen atoms $\equiv\text{Si}-\text{O}^-$ bound with a modifier ion, the O–H bond becomes weaker. This is manifested as a shift of the absorption maximum into the long-wavelength range (3400–3800 nm). The absorption band near 2800 nm corresponds to vibrations in the free (not connected by hydrogen

³ The Dietzel field strength of a cation is Z/a^2 , the ratio of the charge on the cation to the squared cation–anion internuclear distance.

bonds) OH groups, and the band near 3600 nm is due to the vibrations of the O–H bond in the hydroxyl groups connected with nonbridge oxygen atoms by hydrogen bonds. One other absorption band can be seen at 4250 nm in some spectra [5]. This band corresponds to vibrations of hydroxyl groups connected by strong hydrogen bonds which arise when the hydrogen in the hydroxyl groups interacts with the nonbridge oxygen atoms of isolated silicon-oxygen tetrahedra $[\text{Si}(\text{OR})_4]$.

Studies of electronic polarization in glasses have shown that refraction is also sensitive to the amount of impurity water present in the glass. Different authors have observed in borate glasses a different change in the refractive index with increasing H_2O content. The presence of water in glassy boron oxide and binary borate glasses affects the acoustic-loss spectrum [20].

It has been suggested that water present in the structure of sodium-boron glasses decreases the relaxation time of the structure [26].

In most alkali glasses, quite distinct peaks due to the dissipation of mechanical energy are observed in measurements of the temperature dependence of the internal friction (IF). Binary glasses containing only cations of one alkali metal exhibit only one IF peak, whose existence is attributed to the mobility of the alkali-metal cations. Two IF peaks have been observed in silicate and phosphate glasses containing impurity water [20].

The electric conductivity of alkali-tellurite glasses increases as their water content increases [27].

In the last few years it has been determined that the water content in glass increased when the furnace was switched to oxygen blasting. This was attributed to the higher content of water vapor in the atmosphere inside the furnace [28, 29]. This resulted in changes in the color and, as a result of a small decrease of the viscosity of the melt, changes in the glass clarification process. The batch composition must be modified in order to neutralize the effect of oxygen blasting on the properties of glass [30]. Changing the composition of the atmosphere in the furnace increases the foam on the surface of the molted mass and also causes glass to crystallize [31], which degrades its functional properties [32], though under certain conditions the water can “restore” the broken bonds when the glass is worked (cut, pulverized, fragmented, polished, and so on) [33].

Studies of the water content in glass are being resumed. This is especially important for commercial compositions of container and sheet glass. The reasons for this are as follows. In the first place, glass production must meet more stringent quality requirements. In the second place, glass of amorphous modifications of SiO_2 [34], which contain water (hydrothermal batch [35–37], including in autoclave and autoclave-free methods of obtaining liquid glass) is being used in technology. In the third place, prepared batches (briquetted and granular, where water is a binding agent) are being used. Finally, NaOH , $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, $\text{Al}(\text{OH})_3$, and other com-

pounds are being used as raw materials. In addition, the literature does not contain adequate information on the effect of water on the crystallizability of glass, which, together with the viscosity, affects the physical-chemical and technological properties of glass. Little attention has been devoted to the effect of the moisture content of the batch on glass formation and the structural properties of glasses.

This review of the effect of water content on glass-making and final product quality shows that further investigations in this field remain important and necessary because new artificial and natural raw materials are now being used in production and because the oxygen added to burn fuel changes the composition of the atmosphere in the glass-making furnace.

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